Supplementary data

Structures and Properties of 4-phpy, pyz, and 4,4′-bpy Adducts of Lantern-Type Dirhodium Complexes with μ-Formamidinato and μ-Carboxylato Bridges

Makoto Handa[*1], Satoshi Nishiura[1], Makoto Kano[1], Natsumi Yano[1], Haruo Akashi[2], Masahiro Mikuriya[3], Hidekazu Tanaka[1], Tatsuya Kawamoto[4], and Yusuke Kataoka[1]

[1]*Department of Chemistry, Graduate School of Natural Science and Technology, Shimane University, Matsue 690-8504, Japan*

[2]*Institute of Frontier Science and Technology, Okayama University of Science, 1-1 Ridaicho, Kita-Ku, Okayama 700-0005, Japan; akashi@rins.ous.ac.jp*

[3]*Department of Applied Chemistry for Environment and Research Center for Coordination Molecule-based Devices, School of Science and Technology, Kwansei Gakuin University, 2-1 Gakuen, Sanda 669-1337, Japan*

[4]*Department of Chemistry, Faculty of Science, Kanagawa University, 2946 Tsuchiya, Hiratsuka, Kanagawa 259-1293, Japan*

[*]Makoto Handa, e-mail: handam@riko.shimane-u.ac.jp

Table S1 Rh-Rh bond distances of related Rh_2 complexes

Complexes	Rh-Rh / Å	ref.
$Rh_2^{II,II}$		
$[Rh_2(O_2CMe)_4(H_2O)_2]$	2.386(1)	38, 39
$[Rh_2(HNOCMe)_4(H_2O)_2]\cdot 3H_2O$	2.415(1)	43
$[Rh_2(dpf)_4(MeCN)_2]$	2.459(1)	44
$[Rh_2(4\text{-Me-pf})_4]$	2.4336(4)	27
$Rh_2^{II,III}$		
$[Rh_2(O_2CMe)_4(H_2O)_2]ClO_4\cdot H_2O$	2.315(2), 2.318(2)	37
$[Rh_2(HNOCMe)_4(H_2O)_2]ClO_4$	2.3991(1)	40
$[Rh_2(HNOCMe)_4(H_2O)_2]PF_6$	2.4084(10)	41
$[Rh_2(HNOCMe)_4(H_2O)_2]PF_6\cdot 2H_2O$	2.4015(4)	41
$[Rh_2(HNOCMe)_4(H_2O)_2][ReO_4]$	2.4053(7)	42
$[Rh_2(HNOCMe)_4(py)_2]BF_4$	2.434(1)	46
$[Rh_2(dpf)_4(MeCN)_2]ClO_4$	2.466(1)	44
$[Rh_2(4\text{-Me-pf})_4]ClO_4$	2.447(1)	45

dpf^- = *N,N′*-diphenylformamidinate anion

4-Me-pf^- = *N,N′*-bis(4-methylphenyl)formamidinate anion

Table S2 Selected bond distances (Å) and angles (°) concerning Rh_2 cores for **3 –9**

***cis*-[Rh_2(4-Me-pf)$_2$(O_2CCF_3)$_2$(4-phpy)$_2$] (3)**

Rh1-Rh1	2.4702(3)	Rh1-N3	2.3045(17)
Rh1-N1	1.9964(18)	Rh1-O1	2.0966(15)
Rh1-N2	2.0173(17)	Rh1-O2	2.0909(15)
N1-Rh1-N3	101.29(7)	N1-Rh1-N2	91.03(8)
N1-Rh1-O1	174.58(6)	N2-Rh1-O1	87.19(7)
N1-Rh1-O2	87.36 (7)	N2-Rh1-O2	173.85(6)
O1-Rh1-O2	93.88(6)	N2-Rh1-N3	102.10(7)
N3-Rh1-O1	84.09(6)	O2-Rh1-N3	84.04(6)
N1-Rh1-Rh1	87.43(5)	N2-Rh1-Rh1	87.79(5)
O1-Rh1-Rh1	87.39(4)	O2-Rh1-Rh1	86.22(4)
N3-Rh1-Rh1	166.58(5)		

***cis*-[Rh_2(4-Me-pf)$_2$(O_2CCMe_3)$_2$(4-phpy)$_2$] (4)**

Rh1-Rh1	2.4428(4)	Rh1-N3	2.289(2)
Rh1-N1	2.021(3)	Rh1-O1	2.068(2)
Rh1-N2	2.028(2)	Rh1-O2	2.072(2)
N1-Rh1-N3	98.72(9)	N1-Rh1-N2	90.79(11)
N1-Rh1-O1	174.18(8)	N2-Rh1-O1	90.22(9)
N1-Rh1-O2	89.29 (10)	N2-Rh1-O2	174.57(8)
O1-Rh1-O2	89.17(9)	N2-Rh1-N3	100.36(9)
N3-Rh1-O1	86.74(8)	O2-Rh1-N3	85.00(9)
N1-Rh1-Rh1	86.58(7)	N2-Rh1-Rh1	88.95(6)
O1-Rh1-Rh1	87.70(5)	O2-Rh1-Rh1	85.63(5)
N3-Rh1-Rh1	169.17(7)		

***cis*-[Rh_2(4-Me-pf)$_2$(O_2CCMe_3)$_2$(4-ph-py)$_2$]BF_4·2MeOH (5·2MeOH)**

Rh1-Rh2	2.45320(19)	Rh2-N2	1.9719(16)
Rh1-N1	1.9716(16)	Rh2-N4	1.9730 (16)
Rh1-N3	1.9824(16)	Rh2-N6	2.2935(16)
Rh1-N5	2.2673(16)	Rh2-O2	2.0473(13)
Rh1-O1	2.0460(13)	Rh2-O4	2.0455(14)
Rh1-O3	2.0558(14)		
N1-Rh1-N3	94.22(7)	N2-Rh2-N4	94.92(7)

(Table S2 continued)

N1-Rh1-O1	174.39(6)	N2-Rh2-O2	173.79(6)
N1-Rh1-O3	87.88(6)	N2-Rh2-O4	89.06(6)
N3-Rh1-O3	173.87(6)	N4-Rh2-O4	174.28(6)
N3-Rh1-O1	89.31(6)	N4-Rh2-O2	87.94(6)
O1-Rh1-O3	88.18(5)	O2-Rh2-O4	87.71(6)
N1-Rh1-N5	97.97(6)	N2-Rh2-N6	100.49(6)
N3-Rh1-N5	100.49(6)	N4-Rh2-N6	99.62(6)
O1-Rh1-N5	85.64(6)	O4-Rh2-N6	83.65(6)
O3-Rh1-N5	84.89(6)	O2-Rh2-N6	84.43(6)
N5-Rh1-Rh2	168.71(4)	N6-Rh2-Rh1	168.11(4)
N3-Rh1-Rh2	88.15(5)	N2-Rh2-Rh1	88.67(5)
O3-Rh1-Rh2	86.15(4)	O4-Rh2-Rh1	87.88(4)
O1-Rh1-Rh2	87.24(4)	N4-Rh2-Rh1	88.17(5)
N1-Rh1-Rh2	88.53(5)	O2-Rh2-Rh1	86.91(4)

$[Rh_2(4\text{-Me-pf})_2(O_2CCF_3)_2(pyz)]_n$ (6)

Rh1-Rh2	2.464(3)	Rh2-N2	2.012(4)
Rh1-N1	2.027(4)	Rh2-N4	2.021(4)
Rh1-N3	2.016(4)	Rh2-N6	2.320(4)
Rh1-N5	2.301(4)	Rh2-O2	2.111(3)
Rh1-O1	2.095(3)	Rh2-O4	2.086(3)
Rh1-O3	2.106(4)		
N3-Rh1-N1	92.50(18)	N3-Rh1-O1	174.71(14)
N1-Rh1-O1	89.87(17)	N3-Rh1-O3	89.08(17)
N1-Rh1-O3	173.08(12)	O1-Rh1-O3	88.02(16)
N3-Rh1-N5	96.37(14)	N1-Rh1-N5	94.83(16)
O1-Rh1-N5	88.13(13)	O3-Rh1-N5	91.69(14)
N3-Rh1-Rh2	88.48(12)	N1-Rh1-Rh2	86.40(13)
O1-Rh1-Rh2	86.95(10)	O3-Rh1-Rh2	86.91(11)
N5-Rh1-Rh2	174.93(9)	N2-Rh2-N4	92.42(18)
N2-Rh2-O2	89.35(16)	N4-Rh2-O2	173.07(12)
N2-Rh2-O4	174.47(13)	N4-Rh2-O4	89.33(16)
O2-Rh2-O4	88.32(15)	N2-Rh2-N6	97.54(15)
N4-Rh2-N6	93.59(15)	O2-Rh2-N6	92.81(13)

(Table S2 continued)

N4-Rh2-N6	93.59(15)	O2-Rh2-N6	92.81(13)
O4-Rh2-N6	87.59(15)	N2-Rh2-Rh1	88.11(12)
N4-Rh2-Rh1	86.42(12)	O2-Rh2-Rh1	86.94(11)
O4-Rh2-Rh1	86.76(11)	N6-Rh2-Rh1	174.34(9)

$[Rh_2(4\text{-}Me\text{-}pf)_2(O_2CCMe_3)_2(pyz)]_n$ (7)

Rh1-Rh2	2.4421(5)	Rh2-N2	2.039(4)
Rh1-N1	2.017(4)	Rh2-N4	2.013(4)
Rh1-N3	2.032(4)	Rh2-N6	2.283(4)
Rh1-N5	2.302(4)	Rh2-O2	2.074(3)
Rh1-O1	2.069(3)	Rh2-O4	2.060(3)
Rh1-O3	2.073(3)		
N3-Rh1-N1	90.18(16)	N3-Rh1-O1	174.80(13)
N1-Rh1-O1	89.40(14)	N3-Rh1-O3	89.64(14)
N1-Rh1-O3	174.40 (13)	O1-Rh1-O3	90.27(13)
N3-Rh1-N5	104.22(14)	N1-Rh1-N5	100.41(14)
O1-Rh1-N5	80.95(12)	O3-Rh1-N5	85.06(13)
N3-Rh1-Rh2	88.61(10)	N1-Rh1-Rh2	87.34(10)
O1-Rh1-Rh2	86.20(8)	O3-Rh1-Rh2	87.06(8)
N5-Rh1-Rh2	164.86(10)	N2-Rh2-N4	91.54(16)
N2-Rh2-O2	89.02(14)	N4-Rh2-O2	174.69(13)
N2-Rh2-O4	174.79(13)	N4-Rh2-O4	88.75(15)
O2-Rh2-O4	90.21(12)	N2-Rh2-N6	101.66(14)
N4-Rh2-N6	101.45(14)	O2-Rh2-N6	83.60(12)
O4-Rh2-N6	83.38(12)	N2-Rh2-Rh1	88.31(10)
N4-Rh2-Rh1	87.30(10)	O2-Rh2-Rh1	87.44(8)
O4-Rh2-Rh1	86.50(8)	N6-Rh2-Rh1	166.43(10)

$[Rh_2(4\text{-}Me\text{-}pf)_2(O_2CCF_3)_2(4,4'\text{-}bpy)]_n$ (8)

Rh1-Rh2	2.4678(9)	Rh2-N2	2.013(6)
Rh1-N1	2.035(6)	Rh2-N4	2.026(6)
Rh1-N3	2.003(6)	Rh2-N6	2.294(6)
Rh1-N5	2.300(6)	Rh2-O2	2.108(5)
Rh1-O1	2.103(5)	Rh2-O4	2.098(5)

(Table S2 continued)

Rh1-O3	2.099(5)		
N3-Rh1-N1	92.8(2)	N3-Rh1-O1	87.8(2)
N1-Rh1-O1	172.9(2)	N3-Rh1-O3	175.0(2)
N1-Rh1-O3	88.4 (2)	O1-Rh1-O3	90.4(2)
N3-Rh1-N5	94.5(2)	N1-Rh1-N5	100.6(2)
O1-Rh1-N5	86.4(2)	O3-Rh1-N5	90.0(2)
N3-Rh1-Rh2	87.19(17)	N1-Rh1-Rh2	86.68(16)
O1-Rh1-Rh2	86.31(14)	O3-Rh1-Rh2	88.07(14)
N5-Rh1-Rh2	172.43(17)	N2-Rh2-N4	91.7(2)
N2-Rh2-O2	175.2(2)	N4-Rh2-O2	88.1(2)
N2-Rh2-O4	89.8(2)	N4-Rh2-O4	173.1(2)
O2-Rh2-O4	89.9(2)	N2-Rh2-N6	93.7(2)
N4-Rh2-N6	99.9(2)	O2-Rh2-N6	91.0(2)
O4-Rh2-N6	86.7(2)	N2-Rh2-Rh1	88.04(16)
N4-Rh2-Rh1	87.74(16)	O2-Rh2-Rh1	87.18(14)
O4-Rh2-Rh1	85.58(14)	N6-Rh2-Rh1	172.12(15)

$[Rh_2(4\text{-Me-pf})_2(O_2CCMe_3)_2(4,4'\text{-bpy})]_n$ (9)

Rh1-Rh2	2.4660(7)	Rh2-N2	2.029(4)
Rh1-N1	2.022(4)	Rh2-N4	2.029(3)
Rh1-N3	2.013(4)	Rh2-N6	2.297(3)
Rh1-N5	2.303(3)	Rh2-O2	2.071(3)
Rh1-O1	2.056(3)	Rh2-O4	2.071(3)
Rh1-O3	2.066(3)		
N3-Rh1-N1	90.24(16)	N3-Rh1-O1	174.49(12)
N1-Rh1-O1	90.60(13)	N3-Rh1-O3	89.25(15)
N1-Rh1-O3	175.51 (12)	O1-Rh1-O3	89.49(12)
N3-Rh1-N5	100.96(14)	N1-Rh1-N5	100.38(13)
O1-Rh1-N5	84.24(12)	O3-Rh1-N5	84.10(12)
N3-Rh1-Rh2	87.93(10)	N1-Rh1-Rh2	88.28(10)
O1-Rh1-Rh2	86.66(7)	O3-Rh1-Rh2	87.25(8)
N5-Rh1-Rh2	167.48(10)	N2-Rh2-N4	91.12(15)
N2-Rh2-O2	90.53(13)	N4-Rh2-O2	175.02(13)
N2-Rh2-O4	174.44(12)	N4-Rh2-O4	88.74(14)

(Table S2 continued)

O2-Rh2-O4	89.16(12)	N2-Rh2-N6	99.96(13)
N4-Rh2-N6	98.66(13)	O2-Rh2-N6	85.67(11)
O4-Rh2-N6	85.55(12)	N2-Rh2-Rh1	88.07(10)
N4-Rh2-Rh1	88.20(10)	O2-Rh2-Rh1	87.16(8)
O4-Rh2-Rh1	86.37(8)	N6-Rh2-Rh1	169.27(9)

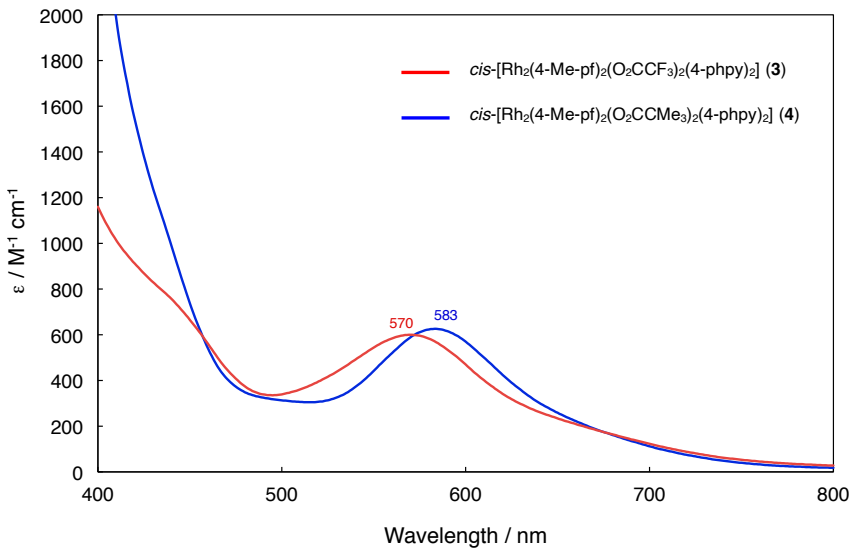

Figure S1. Absorption spectra of *cis*-[Rh_2(4-Me-pf)$_2$(O_2CCF_3)$_2$(4-phpy)$_2$] (**3**) and *cis*-[Rh_2(4-Me-pf)$_2$(O_2CCMe_3)$_2$(4-phpy)$_2$] (**4**) in CH_2Cl_2 at the concentration of 1.0 x 10^{-3} M.

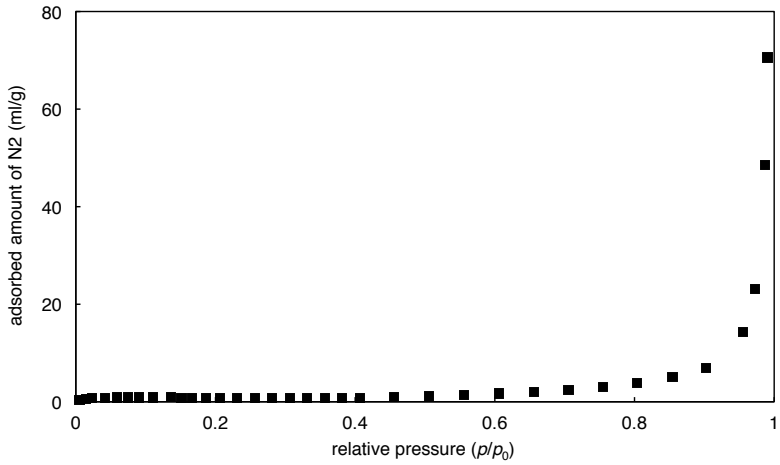

Figure S2. Nitrogen adsorption isotherm of $[Rh_2(4\text{-Me-pf})_2(O_2CCF_3)_2(pyz)]_n$ (**6**).

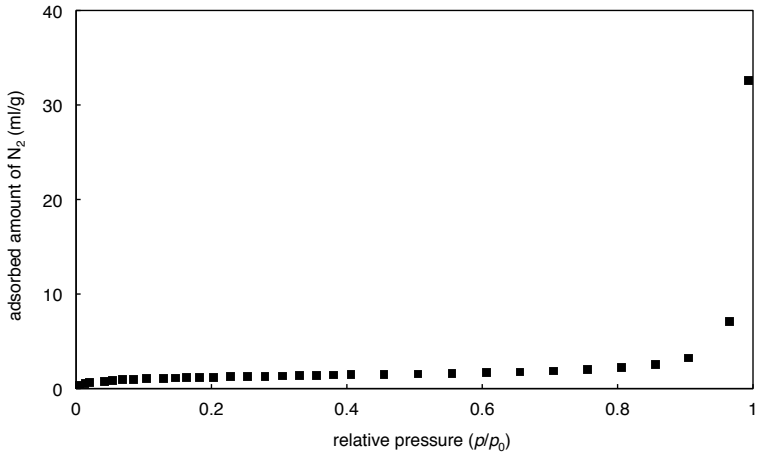

Figure S3. Nitrogen adsorption isotherm of $[Rh_2(4\text{-Me-pf})_2(O_2CCMe_3)_2(4,4'\text{-bpy})]_n$ (**7**).

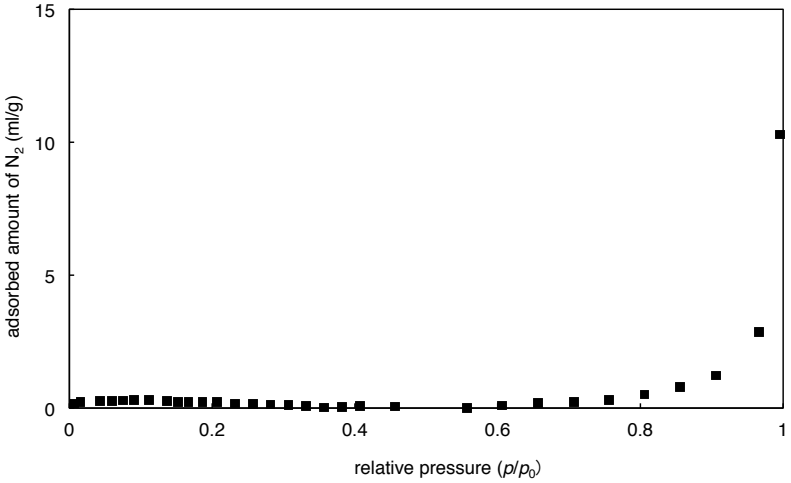

Figure S4. Nitrogen adsorption isotherm of $[Rh_2(4\text{-Me-pf})_2(O_2CCMe_3)_2(4,4'\text{-bpy})]_n$ (**9**).